Polymerization Catalysis

Remote Substituents Controlling Catalytic Polymerization by Very Active and Robust Neutral Nickel(II) Complexes**

*Martin A. Zuideveld, Peter Wehrmann, Caroline Röhr, and Stefan Mecking**

More than 70 million tons of polyethylene and polypropylene are produced annually. The majority is prepared by catalytic polymerization employing Ziegler or Phillips catalysts based on early transition metals. More recently, olefin polymerization by complexes of late transition metals has also received increasing attention.[1] A major motivation is their higher tolerance towards polar reagents due to a reduced oxophilicity by comparison to early transition-metal catalysts. Thus, ethylene and 1-olefins can be copolymerized with acrylates in a random fashion,[2] and ethylene homo- and copolymerizations can be carried out in aqueous emulsion to afford polymer latexes (i.e., aqueous dispersions of polymer particles of about 50–1000 nm size).[3]

The discovery by Brookhart and co-workers of the unique catalytic properties of cationic nickel and palladium diimine catalysts in olefin polymerization has given a strong impulse to the field.[4] As a result, polymerization with neutral Ni^{II} complexes has received renewed interest, as these catalysts are expected to be more functional-group tolerant than their cationic Ni^{II} counterparts. However, catalyst activity and stability over time and the capability to form polymers with higher molecular weights at the same time are critical issues, particularly if the effort for catalyst synthesis is also considered.[5–7] By analogy with the influence of bulky alkyl[4] or aryl[8] groups in cationic diimine complexes, in neutral Ni^{II} κ^2-*N,O* salicylaldiminato complexes bulky isopropyl groups on the *N*-aryl moiety retard chain transfer, which is supported by computational studies by Ziegler and co-workers.[9] Introduction of electron-withdrawing substituents in the *ortho* or *para* position of the *O* donor in neutral nickel(II) complexes has been reported to increase catalytic activities substantially, again in accordance with theoretical calculations.[6c,7a,9] Most specifically for this class of catalysts, Grubbs and co-workers have shown that bulky groups in the C3 position of the *O*-coordinating phenolate moiety of salicylaldimine ligands substantially increase polymerization activity. While these ligands afford highly active catalysts, their syntheses require multistep procedures with very low yields.[6c,d]

Our particular interest in the design of novel Ni^{II} salicylaldiminato complexes stems from the recent finding that the known isopropyl-substituted complexes enable the synthesis of latexes of high-molecular-weight polyethylene, which are, to date, inaccessible by other techniques.[3d] Such polyolefin latexes can provide environmentally friendly and economically attractive coatings, which, for example, can be stable towards UV light and hydrolysis at the same time in contrast to current commodity coatings.[10] In view of applications, a very active catalyst based on conveniently accessible ligands, and that is suited to polymerization in emulsion to higher-molecular-weight polyethylene is a prerequisite. Such a system is equally attractive for fundamental studies of catalytic polymerization in emulsion, in which well-defined catalyst precursors are also desirable. Our investigations subject to this report were initiated by the reasoning that an aryl substituent with strongly electron-withdrawing groups could provide steric bulk and electron withdrawing properties at the same time.

Suzuki coupling[11,8a] provided a convenient synthetic method for the introduction of electron-withdrawing substituted aryl groups in the C2 and C6 position of the aniline aryl ring (Scheme 1). A series of salicylaldimine ligands with systematically varied electronic properties, **1a**–**e**, resulted from the condensation of the corresponding substituted anilines with 3,5-diiodo-salicylaldehyde. The ^{13}C NMR resonances of the compounds were fully assigned by ^{1}H–^{1}H COSY, heteronuclear ^{1}H-^{13}C 2D NMR and ^{1}H–^{13}C 2D long-range-coupling NMR spectroscopy. The chemical shifts of the carbon atom *para* to the imine function in **1a**–**e** (atom labeled *p* in Scheme 1) are $\delta = 126.90$, 126.96, 126.55, 126.48, and 126.56 ppm, respectively, and for the imine carbon atom, C=N, $\delta = 168.42$, 168.05, 166.99, 166.23, and 166.26 ppm were observed. Although the differences in chemical shifts are moderate, this trend follows the electron withdrawing/donating character of the R group and indicates that the electronic character of the substituents R in **1** indeed affects the electronic properties of the neighboring aryl ring and the imine function.

Reaction of **1a**–**e** in diethylether with [(tmeda)-Ni(CH$_3$)$_2$][12] (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) in the presence of excess pyridine[3c,6b,6d,6g] afforded the neutral methylnickel(II) complexes **2a**–**e** in high yield (Scheme 1). The molecular structure of **2a** and **2c** was determined by single-crystal X-ray crystallography (Figure 1).[13,14] To our knowledge, these are the first examples of structurally characterized neutral methylnickel complexes, which are precursors to very active olefin polymerization catalysts. Such methyl complexes are of particular interest, in comparison to the more frequent phenyl complexes[5–7]

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[*] Dr. M. A. Zuideveld, Dipl. Chem. P. Wehrmann,
Priv.-Doz. Dr. S. Mecking
Institut für Makromolekulare Chemie und Freiburger Materialforschungszentrum der Albert-Ludwigs-Universität Freiburg
Stefan-Meier-Strasse 31, 79104 Freiburg (Germany)
Fax: (+49) 761-203-6319
E-mail: stefan.mecking@makro.uni-freiburg.de
Prof. Dr. C. Röhr
Institut für Anorganische Chemie der
Albert-Ludwigs-Universität Freiburg
Albertstrasse 20, 79104 Freiburg (Germany)

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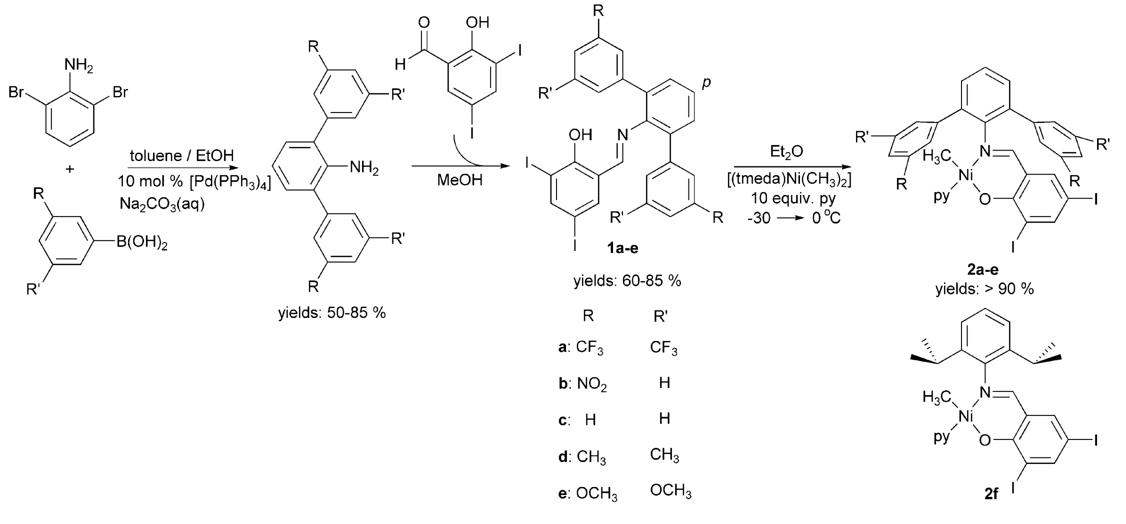

Scheme 1. Synthesis of ligands **1 a**–**e** and of methylnickel(II) complexes **2 a**–**e** (py = pyridine).

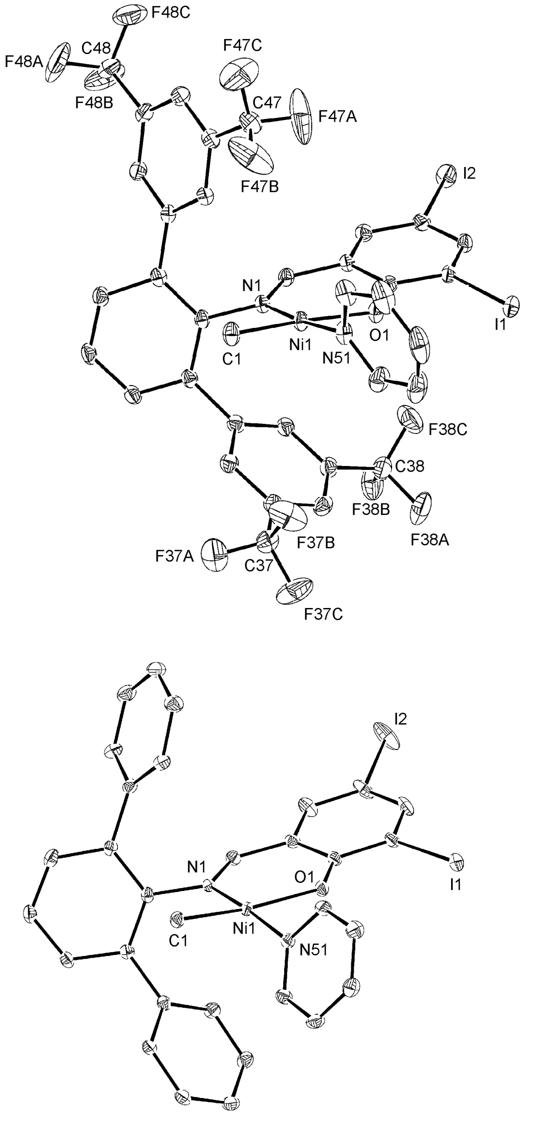

Figure 1. X-ray crystal structure of **2 a** (top) and **2 c** (bottom; ORTEP presentation with thermal ellipsoids drawn at the 50% probability level). Hydrogen atoms are omitted for clarity.

[(XO)NiPh(L)] (X = N or P), as the methyl group resembles the growing polymer chain much more closely than a phenyl group. For example, a hindered activation for polymerization due to slow insertion of ethylene in the Ni–C bond of the catalyst precursor need not be considered.[5e,15] The nickel-bound methyl group is located in the *trans* position to the O donor in both complexes **2 a** and **2 c**. A strong steric shielding of the apical positions of the metal center by the aryl groups bound to the C2,C6-position of the N-aryl moiety is evident for both compounds.

Complexes **2 a**–**e**, and for comparison also the known complex **2 f**,[3c] were employed as precursors for ethylene polymerization (Table 1). Alternatively, the mixing of ligands **1 a**–**f** with one equivalent of [(tmeda)Ni(CH_3)$_2$] in toluene solution under an ethylene atmosphere afforded an in situ catalyst (entry 3), which allowed a convenient rapid prescreening of these and other ligands in automated parallel pressure reactors.[16] The activity of all catalysts with 3,5-substituted aryl moieties (R,R′ = CF_3, Me and OMe; **2 a, 2 d**, and **2 e**) is much higher by comparison to the well-known isopropyl substitution pattern represented by **2 f** (entries 1, 7, 8 and 9). Catalysts formed from **2 b** and **2 c**, which do not bear substituents in the 3,5-position (R,R′ = H) or are only monosubstituted (R = NO_2, R′ = H), respectively, appear much less active. The catalyst stability over time was studied by monitoring the ethylene uptake by means of a mass flow meter. Whereas **2 a**, **2 d**, **2 e**, and **2 f** remain active for hours at 60 °C and 10 bar ethylene pressure, **2 b** and **2 c** are deactivated completely within 20 minutes (see Supporting Information). The initial activities are similar for all five catalysts **2 a**–**e**, and thus the lower average activity of **2 b** and **2 c** in the 30 min experiments given in Table 1 is due to deactivation rather than to a strong difference in intrinsic activity between the five catalysts. Possibly, a deactivation of **2 b** and **2 c** by C–H activation of the hydrogen atom in *meta* position of the phenyl rings occurs.[17] Alternatively, the somewhat higher steric bulk in **2 a**, **2 d**, and **2 e** may prevent possible bimolecular[6d] deactivation reactions. As for the known isopropyl-substituted catalysts,[3c] activities of the aryl-substituted catalysts

Table 1: Results of ethylene polymerization reactions.[a]

Entry	Catalyst precursor (R/R′)	Amount of catalyst [μmol]	Pressure [bar]	Polymer yield [g]	TOF [mol(C_2H_4) mol(Ni)$^{-1}$ h^{-1}][b]	$\bar{M}_n$ [g mol^{-1}][c]	$\bar{M}_w$/$\bar{M}_n$[c]	Branching (per 1000C)[d]	T_m [°C]
1	**2a** (CF_3)	40	40	23.4	41 800	1.9×10^4	5.1	10	123
2	**2a** (CF_3)	19	5	2.2	8270	1.6×10^4	6.7	10	124
3	**1a**[e] (CF_3)	56	5	7.3	9320	3.2×10^4	8.2	14	125
4	**2b** (NO_2)[i]	40	40	3.0	5360	1.1×10^4	2.6	26	106
5	**2c** (H)	40	40	9.0	16 080	2.9×10^3	2.3	52	78
6	**2c** (H)	56	5	2.5	3200	4.0×10^3	2.3	54	68
7	**2d** (Me)	40	40	24.0	42 800	1.1×10^3	2.1	76	–[f]
8	**2e** (OMe)	40	40	25.0	44 600	1.9×10^3	2.5	79	–[f]
9	**2f**	40	40	4.2	7500	1.2×10^4	2.5	5	127
10[g]	**2a** (CF_3)	19	40	3.0[h]	5640	1.8×10^4	3.1	14	122

[a] Reaction conditions: 100 mL of toluene, 50 °C, reaction time 0.5 h. [b] TOF = average turnover frequency. [c] Determined by GPC versus linear polyethylene standards. [d] Branches per 1000 carbon atoms (predominantly methyl branches). [e] In situ catalyst (**1** + [(tmeda)Ni(CH_3)$_2$]). [f] Completely amorphous polymer. [g] Reaction in aqueous emulsion; reaction time 1 h. [h] Formed as an aqueous polymer dispersion. [i] Monosubstituted, R = NO_2, R′ = H.

2a–e are strongly dependant on ethylene concentration (entries 1, 2, 5 and 6).

Surprisingly, despite their spatial remoteness from the metal center the nature of the substituents R,R′ has a dramatic effect on branching and thus crystallinity, and on polymer molecular weight (Table 1). With **2a** a semicrystalline, stiff polymer of 50% crystallinity (determined by differential scanning calorimetry, DSC) is obtained. Complexes **2b** and **2c** afford polyethylenes with a considerably higher degree of branching, and correspondingly low crystallinities (18% and < 10%, respectively), and with **2d** and **2e** an entirely amorphous material is obtained. At the same time, the molecular weight of the polymer decreases by more than an order of magnitude going from **2a** to **2e**. The origin of the relatively broad molecular weight distributions obtained with **2a** is currently unclear. Given the similar intrinsic activities of all catalysts, the lower molecular weight obtained with **2d** and **2e** cannot result from a lower rate of chain growth, but must indeed result from a higher rate of chain transfer. This is also in reasonable accordance with the higher branching observed: methyl branching originates from a β-hydride transfer and a subsequent 2,1-reinsertion of the resulting metal-bound 1-olefin, and β-hydride transfer is also crucial in chain transfer.[18] Whereas the steric requirements of the substituents R,R′ are roughly similar in **2a** (R,R′ = CF_3), **2d** (R,R′ = CH_3) and **2e** (R,R′ = OCH_3) and higher than in **2c** (R,R′ = H),[19] their electron withdrawing character increases in the sequence **2e** ≈ **2d** < **2c** < **2b** ≈ **2a**.[20] Both the molecular weights and the branching of the polymers obtained with these different catalyst precursors vary systematically with the electronic nature of R rather than their steric requirements. This indicates that the effect of these remote substituents is related to their electronic properties. To our knowledge, there is no precedent for such a pronounced and systematic effect of such remote substituents on catalytic olefin polymerization by late transition-metal complexes, despite the enormous recent research efforts directed towards the latter field.[1] Future theoretical studies may provide insight on the correlation of the substitution pattern of the particular ligands and the reactivity of the metal center.

Ethylene polymerization with **2a** in aqueous emulsion was investigated. By comparison to polymerization with the isopropyl-substituted complex **2f**,[3d] activities are increased five-fold in preliminary experiments without further optimization. In experiments with reaction times from 1 to 5 h the polymer yield increased linearly with time, thus demonstrating the robustness of the catalyst system based on **2a** during polymerization in aqueous emulsion (Figure 2).

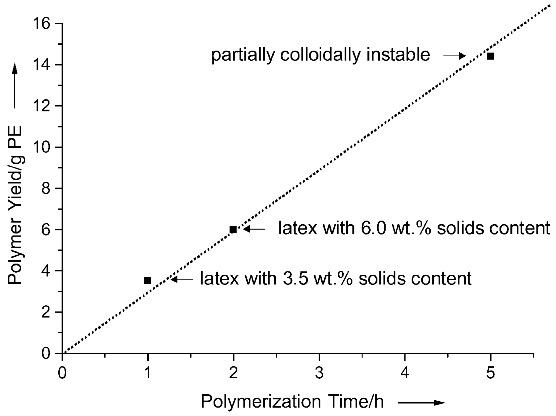

Figure 2. Polymer yield in polymerization in aqueous emulsion with catalyst precursor **2a** (ethylene pressure: 40 bar. Reaction temperature: 50 °C. Dotted line given only as a visual aid).

In summary, we present very active neutral methylnickel(II) complexes for ethylene polymerization based on a set of conveniently accessible ligands. A series of well-defined catalyst precursors with a systematically varied substitution pattern reveals a surprising and unprecedented effect of remote substituents on polymer branching and molecular weight, despite their spatial remoteness from the catalytically active center. An appropriate substitution pattern provides a catalyst that combines the capability to polymerize ethylene to higher-molecular-weight polymer with a high stability and activity in polymerization in aqueous emulsion.

Experimental data is given in the Supporting Information: Synthesis and analytical data (^{1}H and ^{13}C NMR data and elemental analysis) of **1a–e** and **2a–e**; polymerization procedures; investigation on catalyst stability over time for **2a** and **2c** and ORTEP plots of **2a** and **2c** with full labeling schemes.

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[13] Crystallographic data for **2a** and **2c**. **2a**: $C_{35}H_{20}F_{12}I_2N_2NiO$, $M_r = 1025.04$, monoclinic space group $P2_1/c$ (no. 14), $a = 12.840(2)$, $b = 14.681(2)$, $c = 20.919(3)$ Å, $\beta = 113.049(7)°$, $V = 3628.5(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.8764(5)$ g cm^{-3}, $\mu = 23.30$ cm^{-1}, $R1$ (wR_2) = 0.035 (0.100), $T = 293(2)$ K, GOF = 1.031. **2c**: $C_{31}H_{24}I_2N_2NiO$, $M = 753.01$, triclinic space group $P\bar{1}$ (no. 2), $a = 8.460(3)$, $b = 12.243(4)$, $c = 14.917(5)$ Å, $\alpha = 113.380(5)$ $\beta = 90.876(5)°$, $\gamma = 95.868(6)$, $V = 1408.0(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.7762(10)$ g cm^{-3}, $\mu = 29.08$ cm^{-1}, $R1$ ($wR2$) = 0.045 (0.101), $T = 223(2)$ K, GOF = 1.01. The intensity data were collected on a Bruker AXS CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å). The structures were solved by direct methods with SHELXS-97. All hydrogen atoms were refined anisotropically. The final cycles of full-matrix least-squares refinement by using SHELXL-97 were based on 6396 (**2a**) and 6270 (**2c**) observed reflections (all data) and 485 (**2a**) and 340 (**2c**) variable parameters, respectively. CCDC-214669 (**2a**) and CCDC-214670 (**2c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[14] Selected bond lengths (in Å) and angles for **2a**: Ni1-C1 1.931(4); Ni1-N1 1.896(3); Ni1-O 1.908(3); Ni1-N51 1.897(4); N1-Ni1-O1 92.6(1)°; C1-Ni1-N51 87.5(2)°; N1-Ni-C1 96.3(2); O1-Ni1-N51 83.7(1). **2c**: Ni1-C1 1.941(5) Å; Ni1-N1 1.903(4); Ni1-O1 1.920(3); Ni1-N51 1.908(4); N1-Ni1-O1 93.8(1); C1-Ni1-N51 87.3(2); N1-Ni1-C1 95.4(2); O1-Ni1-N51 84.7(2).

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